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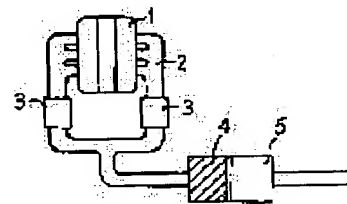
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(54) ADSORBING CATALYST FOR PURIFYING EXHAUST GAS

(57)Abstract:

PURPOSE: To efficiently remove high concn. hydrocarbon using an adsorbing catalyst obtained by forming a catalyst layer consisting of a powder based on activated ceria and/or alumina and a catalytic component selected from Pt, Pd and Rh on a zeolite layer.

CONSTITUTION: An exhaust gas purifying device is formed by arranging a Pt-Rh catalyst to the exhaust manifold 2 of an engine 1 as a preternary catalyst 3 and providing an adsorbing catalyst 4 in front of the Pt-Rh catalyst 4 of an under-floor catalyst 5. This adsorbing catalyst 4 is obtained by providing a catalyst layer wherein at least one kind of an element selected from a group consisting of Pt, Pd and Rh is added to a powder based on activated ceria and/or alumina on a zeolite layer.



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CLAIMS

[Claim(s)]

[Claim 1] The adsorption catalyst for emission gas purification by which it is having catalyst bed containing at least one sort chosen from group which becomes powder which used activity Seria and/or alumina as principal component on said zeolite layer from Pt, Pd, and Rh as catalyst component in adsorption catalyst which coated catalyst support with zeolite characterized.

[Claim 2] The adsorption catalyst for emission gas purification according to claim 1 characterized by being at least one sort chosen from the group which a zeolite becomes from mordenite, USY, beta-zeolite, and ZSM-5.

[Claim 3] For a zeolite, mordenite, beta-zeolite, and ZSM-5 are SiO₂ / aluminum 2O₃. It is the range of 50-2000 in a mole ratio, and USY is SiO₂ / aluminum 2O₃. Adsorption catalyst for emission gas purification according to claim 1 or 2 characterized by being the range of 50-300 in a mole ratio.

[Claim 4] The adsorption catalyst for emission gas purification according to claim 1, 2, 3, or 4 characterized by carrying out the isomorphism permutation of the zeolite with one or more sorts in Ag and/or Pd.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the adsorption catalyst for emission gas purification which can remove efficiently the high-concentration hydrocarbon discharged at the time of engine starting about the adsorption catalyst for emission gas purification.

[0002]

[Description of the Prior Art] Conventionally, as a catalyst for emission gas purification of internal combustion engines, such as an automobile, the catalyst which performs oxidation of a carbon monoxide (CO) and a hydrocarbon (HC) and reduction of nitrogen oxides (NO_x) to coincidence is used widely. As such a catalyst, the thing which made the alumina coat layer on fireproof support support noble metals, such as Pd, Pt, and Rh, the thing which added base metal oxides, such as rare earth metals, such as Ce and La, and nickel, as a co-catalyst component if needed are proposed (JP, 58-20307, B). The catalyst indicated by this patent official report is strongly influenced of exhaust gas temperature and an engine setting air-fuel ratio.

[0003] On the other hand, generally 300 degrees C or more of catalysts for automobiles are required for the exhaust gas temperature which demonstrates a purification function, and a catalyst commits an air-fuel ratio most effectively near the theoretical air fuel ratio (A/F=14.6) which can balance oxidization of a hydrocarbon and a carbon monoxide, and reduction of nitrogen oxides. Therefore, by automobile furnished with the exhaust gas purge using the conventional three way component catalyst, it is installed in a location which a three way

component catalyst commits effectively, and the oxygen density of an exhaust air system is detected, and feedback control is performed so that gaseous mixture may be maintained near theoretical air fuel ratio.

[0004] However, even if it was the case where the conventional three way component catalyst was installed immediately after an exhaust manifold, immediately after engine starting with low (300 degrees C or less) exhaust gas temperature, catalytic activity was low and the hydrocarbon discharged in large quantities immediately after starting (at the time of a cold start) had the fault of being discharged as it is, without being purified. In order to solve this fault, the exhaust gas purge which has arranged the hydrocarbon trapper which filled up the exhaust air upstream of a catalytic converter with the adsorption material for adsorbing a cold hydrocarbon is proposed (JP,2-135126,A, JP,3-141816,A).

[0005]

[Problem(s) to be Solved by the Invention] However, in the exhaust gas purge concerning above-mentioned JP,2-135126,A, since the zeolite had sunk in the catalyst metal solution while a hydrocarbon will be desorbed from the adsorption material of the upstream before a catalyst reaches activity temperature since the catalyst component is sunk into the downstream of adsorption material, the endurance of a catalyst component had the fault of being scarce.

[0006] Moreover, in the exhaust gas purge concerning JP,3-141816,A, since desorption control of the hydrocarbon to which it stuck was performed using the temperature sensor, the by-path pipe, the control unit, etc., the system was complicated, it was lacking in dependability and it had the flume fault which is not practical on the exhaust air layout.

[0007] Therefore, the purpose of this invention is to offer the adsorption catalyst for emission gas purification which can remove efficiently the high-concentration hydrocarbon discharged at the time of engine starting.

[0008]

[Means for Solving the Problem and its Function] this invention persons reached [that the high-concentration hydrocarbon discharge at the time of engine starting is efficiently removable , and] a header and this invention by use the adsorption catalyst for emission gas purification which has a catalyst bed containing at least one sort chose from the group which becomes the powder which used activity Seria and/or an alumina as the principal component on the zeolite layer from Pt , Pd , and Rh as a catalyst component as a result of inquire wholeheartedly , in order to solve the above-mentioned technical problem .

[0009] The above-mentioned purpose of this invention was attained in the adsorption catalyst which coated catalyst support with the zeolite by the adsorption catalyst for emission gas purification by which it is having-catalyst bed containing at least one sort chosen from group which becomes powder which used activity Seria and/or alumina as principal component on said zeolite layer from Pt, Pd, and Rh as catalyst component characterized. Hereafter, this invention is further explained to a detail.

[0010] This invention prepares the 1st layer which consists of a zeolite effective in adsorbing a hydrocarbon on catalyst support, as mentioned above. Activity Seria and/or an alumina as a catalyst component to the powder used as the principal component on this 1st layer Furthermore, Pt, The self-consecration mold adsorption catalyst A which prepared the catalyst bed containing at least one sort chosen from the group which consists of Pd and Rh to an exhaust air inflow side It is the adsorption catalyst for emission gas purification characterized by having arranged the catalyst B which coated the three way component catalyst which purifies a hydrocarbon, a carbon monoxide, and nitrogen oxides to the exhaust air outflow side, respectively.

[0011] Since the catalyst bed supported on the zeolite layer is heated earlier than a zeolite layer, the catalyst bed is activated in the phase where a hydrocarbon is desorbed from a zeolite layer, and the adsorption catalyst A by the side of an inflow purifies a hydrocarbon good. Moreover, purification of the hydrocarbon which was not able to be purified by the catalyst bed by the side of an inflow, a carbon monoxide, and nitrogen oxides can be improved by arranging Catalyst B to an outflow side. The hydrocarbon discharged especially at the time of engine starting is efficiently removable among exhaust gas with this.

[0012] Although it can be used choosing suitably from well-known zeolites as a zeolite used in this invention, it is desirable especially to choose from ordinary temperature what has sufficient hydrocarbon adsorption capacity and has high endurance even if it is comparatively high temperature and is moreover under a water existence ambient atmosphere. It is desirable to use at least one sort chosen from the group which consists of mordenite, USY, a beta-zeolite, and ZSM-5, for example as such a zeolite. For mordenite, beta-zeolite, and ZSM-5, the range of 50-2000 and USY are SiO₂ / aluminum 2O₃ at SiO₂ / aluminum² O₃ mole ratio especially. It is desirable that it is the range of 50-300 in a mole ratio. Mordenite, beta-zeolite, ZSM-5, and USY are SiO₂ / aluminum 2O₃. If it becomes less than 50 by the mole ratio, adsorption inhibition of the water molecule which lives together in exhaust gas is serious, and cannot adsorb a hydrocarbon effectively. Conversely, if 2000 is exceeded by the mole ratio and USY exceeds [mordenite, beta-zeolite, and ZSM-5] 300 by the mole ratio, respectively, the amount of adsorption of a hydrocarbon will decrease. By mixing two or more sorts of zeolites

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with which pore size differs from pore structure, the hydrocarbon of the varieties in exhaust gas is efficiently absorbable.

[0013] In this way, although only the adsorption catalyst obtained can fully adsorb a hydrocarbon, in order to equip an exhaust air system and to put in practical use, it is desirable to consider as the self-consecration type to which the engine performance which purifies the hydrocarbon from which it is desorbed with the rise of temperature was added and which coated the three way component catalyst layer on the adsorption layer (zeolite). That is, in this invention, the powder which used activity Seria and/or an alumina as the principal component can be applied on a zeolite layer, and it can have a catalyst bed containing at least one sort chosen from the group which consists of Pt, Pd, and Rh as a catalyst component on the powder further.

[0014] Although various zeolites have adsorption capacity force sufficient also in H mold, they can raise an adsorption property and desorption control ability further by supporting Pd, Ag, Cu, Cr, Co, Nd, etc. using the usual approaches, such as an ion-exchange method, the sinking-in method, and dip coating. Although especially the amount of support of each noble metals is not restricted, it is desirable that it is 0.1 – 15% of the weight of the range. If the amount of support becomes less than 0.1% of the weight, an adsorption property and desorption control ability will fall and, as for the effectiveness beyond it, ** conversely exceeding 15 % of the weight will not be obtained, either.

[0015] Although especially the distance of the adsorption catalyst A by the side of an inflow and the catalyst B by the side of an outflow is not restricted, if too near, the engine performance degradation by back pressure rise may be caused, and if it separates too much conversely, the rate of purification of the hydrocarbon from which the temperature of Catalyst B did not go up, but it was desorbed, a carbon monoxide, and nitrogen oxides may fall. Therefore, as for the distance of Catalyst A and the adsorption catalyst B, it is desirable to consider as the range of 10–50mm.

[0016] It can be used in this invention, choosing suitably from well-known catalyst support as catalyst support, for example, monolith support, metal support, etc. are mentioned. Although not restricted, as for especially the configuration of this catalyst support, it is desirable to usually use it in a honeycomb configuration, and it applies catalyst powder to various honeycomb-like base materials, and is used for them. As this honeycomb material, although many things of the quality of cordierite are generally used, it is also possible to use the honeycomb which consists of a metallic material, and the catalyst powder itself may be further fabricated in a honeycomb configuration. By making the configuration of a catalyst into the shape of a honeycomb, since the touch area of a catalyst and exhaust gas becomes large and pressure loss is also suppressed, when using as an object for automobiles, it is very advantageous.

[0017] [Example] Hereafter, this invention is further explained in full detail according to an example. Unless it refuses especially in an example, the section shows the weight section.

[0018] The activity Seria powder (henceforth Pt/CeO₂) 100 section which supported example 1Pt, the alumina 50 section, and the 2% nitric-acid 150 section were supplied to the magnetic pot, preferential grinding was carried out for 40 minutes or with universal ball mill equipment with vibration mill equipment for 6.5 hours, and the wash coat slurry was manufactured. After carrying out water absorption processing of the monolith support made from cordierite by the suction coat method, said manufactured slurry was supplied so that it might become homogeneity in the whole support cross section, and the excessive slurry was removed by the suction coat method. Subsequently, after drying, temporary baking was carried out at 400 degrees C for 1 hour. Thereby, it is Pt/CeO₂. The coat of the layer was carried out to support in the amount of 100 g/L coats. The above-mentioned wash coat, desiccation, and baking are repeated further, and it is Pt/CeO₂ of a total of 200 g/L. The coat of the layer was carried out. Next, the alumina powder (henceforth Rh/aluminum₂ O₃) 100 section which supported Rh, Supply the alumina 50 section and the 2% nitric-acid 150 section to a magnetic pot, and a wash coat slurry is manufactured like the above. It is Pt/CeO₂ with the same approach. It is Rh/aluminum₂ O₃ of 50 g/L on a layer. The coat of the catalyst bed was carried out, after drying, baking was performed at 650 degrees C under the air ambient atmosphere for 3 hours, and the catalyst 1 by the side of an exhaust air outflow was acquired. Moreover, the H mold ZSN-5 (SiO₂/aluminum₂ O₃ =700) 100 section, the silica sol (20% of solid content) 215 section, the 10% nitric-acid 100 section, and the water 15 section were supplied to the magnetic pot, ZSM-5 slurry was manufactured like the above, and after carrying out the coat of 150 g/L and drying on monolith support by this approach, baking was performed at 400 degrees C for 1 hour. It is Pt/CeO₂ of 100 g/L on ZSM-five layers like the above. The coat of the catalyst bed was carried out, and after drying, baking was performed at 400 degrees C for 1 hour. Furthermore, it is Rh/aluminum₂ O₃ on Pt/CeO two-layer. 50 g/L coat of the catalyst bed was carried out, after drying, baking of 3 hours was performed at 650 degrees C under the air ambient atmosphere, and the adsorption catalyst 1 by the side of an exhaust air inflow was acquired. The adsorption catalyst 1 was combined with the exhaust air inflow side, the catalyst 1 was combined with the

exhaust air outflow side, respectively, and the tandem-die adsorption catalyst 1 was acquired.

[0019] It is Pt/CeO₂ as an example 2 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 2 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 2 by the completely same approach as an example 1, and acquired this

adsorption catalyst 2 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.
[0020] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 3 zeolite, and used the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 50 section and the H mold USY(SiO₂/aluminum 2 O₃ =50)50 section, and also The tandem-die adsorption catalyst 3 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 3 by the completely same approach as an example 1, and acquired this adsorption catalyst 3 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0021] It is Pt/CeO₂ as an example 4 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 4 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 4 by the completely same approach as an example 3, and acquired this adsorption catalyst 4 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0022] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 5 zeolite, and used the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 67 section and the H mold USY(SiO₂/aluminum 2 O₃ =50)33 section, and also The tandem-die adsorption catalyst 5 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 5 by the completely same approach as an example 1, and acquired this adsorption catalyst 5 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0023] It is Pt/CeO₂ as an example 6 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 6 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 6 by the completely same approach as an example 5, and acquired this adsorption catalyst 6 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0024] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 7 zeolite, and used the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 50 section and the H mold mordenite (SiO₂/aluminum 2 O₃ =200) 50 section, and also The tandem-die adsorption catalyst 7 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 7 by the completely same approach as an example 1, and acquired this adsorption catalyst 7 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0025] It is Pt/CeO₂ as an example 8 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 8 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 8 by the completely same approach as an example 7, and acquired this adsorption catalyst 8 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0026] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 9 zeolite, and used the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 50 section and the H mold beta zeolite (SiO₂/aluminum 2 O₃ =100) 50 section, and also The tandem-die adsorption catalyst 9 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 9 by the completely same approach as an example 1, and acquired this adsorption catalyst 9 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0027] It is Pt/CeO₂ as an example 10 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 10 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 10 by the completely same approach as an example 9, and acquired this adsorption catalyst 10 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0028] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 11 zeolite, and used the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 67 section and the H mold beta zeolite (SiO₂/aluminum 2 O₃ =100) 33 section, and also The tandem-die adsorption catalyst 11 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 11 by the completely same approach as an example 1, and acquired this adsorption catalyst 11 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0029] It is Pt/CeO₂ as an example 12 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 12 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 12 by the completely same approach as an example 12, and acquired this adsorption catalyst 12 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0030] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 13 zeolite, and used the H mold USY(SiO₂/aluminum 2 O₃ =50)100 section, and also The tandem-die adsorption catalyst 13 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 13 by the completely same approach as an example 1, and acquired this adsorption catalyst 13 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0031] It is Pt/CeO₂ as an example 14 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 14 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 14 by the completely same approach as an example 13, and acquired this adsorption catalyst 14 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0032] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 15 zeolite, and used the H mold beta zeolite (SiO₂/aluminum 2 O₃ =100) 100 section, and also The tandem-die adsorption catalyst 15 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 15 by the completely same approach as an example 1, and acquired this adsorption catalyst 15 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0033] It is Pt/CeO₂ as an example 16 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 16 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 16 by the completely same approach as an example 15, and acquired this adsorption catalyst 16 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0034] Replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 17 zeolite, and used the H mold mordenite (SiO₂/aluminum 2 O₃ =200) 100 section, and also The tandem-die adsorption catalyst 17 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 17 by the completely same approach as an example 1, and acquired this adsorption catalyst 17 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0035] It is Pt/CeO₂ as an example 18 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 18 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 18 by the completely same approach as an example 17, and acquired this adsorption catalyst 18 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0036] It replaces with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 19 zeolite. The H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 34 section, Used the H mold USY(SiO₂/aluminum 2 O₃ =50)33 section and the H mold mordenite (SiO₂/aluminum 2 O₃ =200) 33 section, and also The tandem-die adsorption catalyst 19 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 19 by the completely same approach as an example 1, and acquired this adsorption catalyst 19 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0037] It is Pt/CeO₂ as an example 20 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 20 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 20 by the completely same approach as an example 19, and acquired this adsorption catalyst 20 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0038] It replaces with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 21 zeolite. The H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 34 section, Used the H mold USY(SiO₂/aluminum 2 O₃ =50)33 section and an H mold beta zeolite, and also The tandem-die adsorption catalyst 21 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 21 by the completely same approach as an example 1, and acquired this adsorption catalyst 21 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0039] It is Pt/CeO₂ as an example 22 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 22 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 22 by the completely same approach as an example 21, and acquired this adsorption catalyst 22 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0040] ZSM-5 which replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 23 zeolite, and carried out the ion exchange of the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 34 section and Ag (henceforth Ag support ZSM-5) The tandem-die adsorption catalyst 23 was acquired combining respectively the catalyst 1 which the SiO₂ / 5 % of the weight [of the amounts of Ag support] and aluminum 2 O₃ =30 33 section and the H mold USY(SiO₂/aluminum 2 O₃ =50)33 section were used, and also acquired the adsorption catalyst 23 by the completely same approach as an example 1, and acquired this adsorption catalyst 23 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0041] It is Pt/CeO₂ as an example 24 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 24 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 24 by the completely same approach as an example 23, and acquired this adsorption catalyst 24 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0042] ZSM-5 which replaced with the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 100 section as example 25 zeolite, and carried out the ion exchange of the H mold ZSM-5 (SiO₂/aluminum 2 O₃ =700) 34 section and the Pd (henceforth Pd support ZSM-5) The tandem-die adsorption catalyst 23 was acquired combining respectively the catalyst 1 which the SiO₂ / 2 % of the weight [of the amounts of Pd support] and aluminum 2 O₃ =30 33

section and the H mold USY(SiO₂/aluminum₂ O₃=50)33 section were used, and also acquired the adsorption catalyst 23 by the completely same approach as an example 1, and acquired this adsorption catalyst 23 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0043] It is Pt/CeO₂ as an example 26 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 26 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 26 by the completely same approach as an example 25, and acquired this adsorption catalyst 26 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0044] It replaces with the H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 100 section as example 27 zeolite. The H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 34 section, Used the Ag support ZSM-5 (5 % of the weight [of the amounts of Ag support], SiO₂/aluminum₂ O₃ =30) 33 section, and the H mold beta zeolite (SiO₂/aluminum₂ O₃ =100) 33 section, and also The tandem-die adsorption catalyst 27 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 27 by the completely same approach as an example 1, and acquired this adsorption catalyst 27 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0045] It is Pt/CeO₂ as an example 28 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 28 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 28 by the completely same approach as an example 27, and acquired this adsorption catalyst 28 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0046] It replaces with the H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 100 section as example 29 zeolite. The H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 34 section, Used the Pd support ZSM-5 (2 % of the weight [of the amounts of Pd support], SiO₂/aluminum₂ O₃ =30) 33 section, and the H mold beta zeolite (SiO₂/aluminum₂ O₃ =100) 33 section, and also The tandem-die adsorption catalyst 29 was acquired combining respectively the catalyst 1 which acquired the adsorption catalyst 29 by the completely same approach as an example 1, and acquired this adsorption catalyst 29 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0047] It is Pt/CeO₂ as an example 30 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 30 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 30 by the completely same approach as an example 29, and acquired this adsorption catalyst 30 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0048] USY which replaced with the H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 100 section as example 31 zeolite, and carried out the ion exchange of the H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 50 section and Ag (henceforth the Ag support USY) The tandem-die adsorption catalyst 31 was acquired combining respectively the catalyst 1 which the SiO₂ / 5 % of the weight [of the amounts of Ag support] and aluminum₂ O₃ =12 50 section was used, and also acquired the adsorption catalyst 31 by the completely same approach as an example 1, and acquired this adsorption catalyst 31 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0049] It is Pt/CeO₂ as an example 32 catalyst component. It replaces with and is Pd/aluminum 2O₃. The tandem-die adsorption catalyst 32 was acquired combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 32 by the completely same approach as an example 31, and acquired this adsorption catalyst 32 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0050] It is Pd/CeO₂ with the same approach as example 33 example 1. The 200 g/L coat of the layer was carried out, and baking was performed after drying. Furthermore, it is Pd/CeO₂ with the same approach. After carrying out 50 g/L coat of the 2O₃ layer of Rh/aluminum and drying on a layer, baking was performed at 650 degrees C under the air ambient atmosphere for 3 hours, and the catalyst 2 was acquired. The adsorption catalyst 5 was combined with the exhaust air inflow side, the catalyst 2 was combined with the exhaust air outflow side, respectively, and the tandem-die adsorption catalyst 33 was acquired.

[0051] The adsorption catalyst 9 was combined with the example 34 exhaust-air inflow side, the catalyst 2 was combined with the exhaust air outflow side, respectively, and the tandem-die adsorption catalyst 34 was acquired.

[0052] It is Pt/CeO₂ as an example 35 catalyst component. It replaces with and is Pt/CeO₂. And the tandem-die adsorption catalyst 35 was acquired, combining respectively the catalyst 1 which Pd/aluminum 2O₃ was used, and also acquired the adsorption catalyst 35 by the completely same approach as an example 3, and acquired this adsorption catalyst 35 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0053] As example 36 zeolite It replaces with the H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 50 section and the H mold USY(SiO₂/aluminum₂ O₃ =50)50 section. The H mold ZSM-5 (SiO₂/aluminum₂ O₃ =700) 67 section and the H mold USY(SiO₂/aluminum₂ O₃=50)37 section The tandem-die adsorption catalyst 36 was acquired

combining respectively the catalyst 1 which it used, and also acquired the adsorption catalyst 36 by the completely same approach as an example 35, and acquired this adsorption catalyst 36 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0054] The example of comparison 1H mold USY(SiO₂/aluminum₂ O₃ =50)100 section, the silica sol (20% of solid content) 215 section, the 10% nitric-acid 100 section, and the water 15 section were supplied to the magnetic pot, the wash coat slurry was manufactured by the completely same approach as an example 1, 150g / L quart, desiccation, and baking were performed to monolith support by this coat approach, and the adsorption catalyst 37 was acquired. The adsorption catalyst 37 was combined with the exhaust air inflow side, the catalyst 1 was combined with the exhaust air outflow side, respectively, and the tandem-die adsorption catalyst 37 was acquired.

[0055] The tandem-die adsorption catalyst 38 was acquired combining respectively the catalyst 1 which replaced with the example of comparison 2H mold USY (SiO₂/aluminum₂ O₃ =50), and the H mold USY (SiO₂/aluminum₂ O₃ =7) was used, and also acquired the adsorption catalyst 38 by the completely same approach as the example 1 of a comparison, and acquired this adsorption catalyst 38 in the example 1 to the exhaust air inflow side at the exhaust air outflow side.

[0056] The following evaluation conditions estimated HC adsorption / washing property using the tandem-die adsorption catalyst acquired in the example examples 1-34 of a trial, and the examples 1-2 of a comparison. The result is shown in Tables 1, 2, and 3.

[0057]

[Table 1]

	触媒番号	HC低減率 Abag 0~125 秒	HC低減率 Abag 0~505 秒
実施例 1	吸着触媒 1	38.8%	6.1%
実施例 2	同 2	38.8%	6.4%
実施例 3	同 3	51.3%	15.2%
実施例 4	同 4	51.3%	17.6%
実施例 5	同 5	51.8%	15.5%
実施例 6	同 6	51.8%	17.7%
実施例 7	同 7	41.7%	13.0%
実施例 8	同 8	41.7%	13.3%
実施例 9	同 9	51.9%	17.7%
実施例 10	同 10	51.9%	17.8%
実施例 11	同 11	52.3%	17.9%
実施例 12	同 12	52.3%	18.1%
実施例 13	同 13	39.4%	12.9%
実施例 14	同 14	39.4%	13.1%
実施例 15	同 15	45.0%	15.1%
実施例 16	同 16	45.0%	15.3%
実施例 17	同 17	39.0%	9.0%

[0058]

[Table 2]

	触媒番号	H C 低減率	H C 低減率
実施例 18	吸着触媒 18	39.0%	9.1%
実施例 19	同 19	52.0%	15.1%
実施例 20	同 20	52.0%	15.2%
実施例 21	同 21	52.5%	18.1%
実施例 22	同 22	52.5%	18.2%
実施例 23	同 23	52.9%	18.5%
実施例 24	同 24	52.9%	18.6%
実施例 25	同 25	51.4%	15.3%
実施例 26	同 26	51.4%	17.7%
実施例 27	同 27	53.1%	18.9%

[0059]

[Table 3]

	触媒番号	H C 低減率	H C 低減率
実施例 28	吸着触媒 28	53.1%	18.9%
実施例 29	同 29	51.5%	15.3%
実施例 30	同 30	51.4%	15.3%
実施例 31	同 31	52.0%	15.4%
実施例 32	同 32	52.0%	15.6%
実施例 33	同 33	51.8%	16.8%
実施例 34	同 34	51.9%	17.9%
実施例 35	同 35	51.3%	16.5%
実施例 36	同 36	51.3%	14.8%
比較例 1	同 37	39.4%	0%
比較例 2	同 38	2.0%	0%

[0060] In addition, as shown in drawing 1 in evaluation, the Pt-Ph system catalyst has been arranged as a Puri three way component catalyst 3 (0.5L) to the exhaust manifold 2 of an engine 1, and the adsorption catalyst non-equipped a case and an engine-performance comparison were performed using the exhaust gas purge which equipped with the adsorption catalyst 4 (1.3L) before the Pt-Rh system catalyst of the under floor catalyst 5 (1.3L). In order to evaluate the adsorption capacity of the hydrocarbon discharged at the time of (1) engine starting in evaluation, the rate of emission reduction for Abag0 - 125 seconds was measured.

(2) Before the three way component catalyst of an adsorption catalyst lower stream of a river also activates the hydrocarbon to which it stuck temporarily, ****. There is no emission reduction effectiveness. Then, in order to evaluate the desorption control ability and self-consecration ability by the adsorption catalyst, the rate of emission reduction for [Abag] 0 - 505 seconds was measured.

[0061] Evaluation condition catalyst capacity 1.3L evaluation car The Nissan Motor Co., Ltd. make, 300 cc engine evaluation mode of V type 6-cylinder LA4-CH (Abag)

Hydrocarbon carbon number discharged at the time of engine starting (inside of the gas of a catalyst inlet port) C2 - C3 21.2% (C1 it removes by **) C4 - C6 33.0% C7 - C9 45.8% [0062]

[Effect of the Invention] The adsorption catalyst for emission gas purification of this invention can remove efficiently the high-concentration hydrocarbon discharged at the time of engine starting by arranging the adsorption catalyst by which the coat of the catalyst bed was carried out on the adsorption layer effective in hydrocarbon adsorption on catalyst support to an exhaust air inflow side, and arranging the catalyst which carried out the coat of the inorganic substance which contains a catalytic activity component on catalyst support to an exhaust air outflow side.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram of the exhaust gas purge used for the example of a trial.

[Description of Notations]

- 1 Engine
- 2 Exhaust Manifold
- 3 Puri Three Way Component Catalyst
- 4 Adsorption Catalyst
- 5 Under Floor Three Way Component Catalyst

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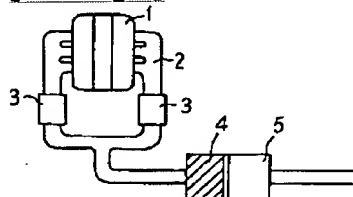
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DRAWINGS

[Drawing 1]



[Translation done.]

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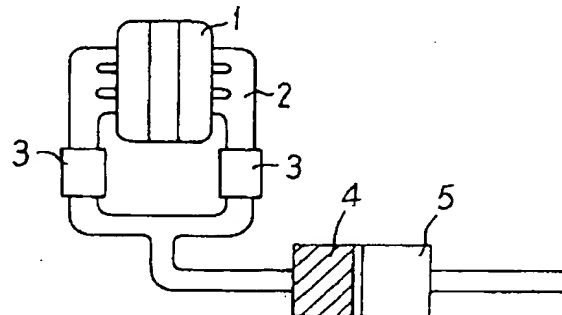
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(54) 【発明の名称】 排ガス浄化用吸着触媒

(57) 【要約】

【目的】 エンジン始動時に排出される高濃度の炭化水素を効率良く除去することのできる排ガス浄化用吸着触媒を提供すること。

【構成】 触媒担体にゼオライトをコーティングした吸着触媒において、前記ゼオライト層上に活性セリア及び／又はアルミナを主成分とした粉末に触媒成分として P t、P d 及び R h からなる群から選ばれた少なくとも1種を含む触媒層を有すること特徴とする排ガス浄化用吸着触媒。



【特許請求の範囲】

【請求項1】 触媒担体にゼオライトをコーティングした吸着触媒において、前記ゼオライト層上に活性セリア及び／又はアルミナを主成分とした粉末に触媒成分としてPt、Pd及びRhからなる群から選ばれた少なくとも1種を含む触媒層を有すること特徴とする排ガス浄化用吸着触媒。

【請求項2】 ゼオライトがモルデナイト、USY、 β -ゼオライト及びZSM-5からなる群から選ばれた少なくとも1種であることを特徴とする請求項1記載の排ガス浄化用吸着触媒。

【請求項3】 ゼオライトがモルデナイト、 β -ゼオライト及びZSM-5が $\text{SiO}_2/\text{Al}_2\text{O}_3$ 、モル比で50～2000の範囲であり、USYが $\text{SiO}_2/\text{Al}_2\text{O}_3$ 、モル比で50～300の範囲であることを特徴とする請求項1又は2記載の排ガス浄化用吸着触媒。

【請求項4】 ゼオライトがAg及び／又はPdのうち1種以上と同型置換されたことを特徴とする請求項1、2、3又は4記載の排ガス浄化用吸着触媒。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、排ガス浄化用吸着触媒に関し、特に、エンジン始動時に排出される高濃度の炭化水素を効率良く除去することのできる排ガス浄化用吸着触媒に関する。

【0002】

【従来技術】従来、自動車等の内燃機関の排ガス浄化用触媒としては、一酸化炭素(CO)及び炭化水素(HC)の酸化と、窒素酸化物(NO_x)の還元とを同時に行う触媒が汎用されている。このような触媒としては、耐火性担体上のアルミナコート層に、Pd、Pt、Rh等の貴金属を担持させたもの、及び必要に応じて助触媒成分としてCe、La等の希土類金属やNi等のベースメタル酸化物を添加したもの等が提案されている(特公昭58-20307号公報)。この特許公報に記載されている触媒は、排ガス温度及びエンジンの設定空燃比の影響を強く受ける。

【0003】一方、自動車用触媒が浄化機能を発揮する排ガス温度は、一般に300℃以上必要であり、また空燃比は、炭化水素及び一酸化炭素の酸化と窒素酸化物の還元とのバランスがとれる理論空燃比($A/F=14.6$)付近で触媒が最も有効に働く。従って、従来の三元触媒を用いる排ガス浄化装置を取り付けた自動車では、三元触媒が有効に働くような位置に設置されており、また排気系の酸素濃度を検出して、混合気を理論空燃比付近に保つようにフィードバック制御が行われている。

【0004】しかしながら、従来の三元触媒をエキゾーストマニホールド直後に設置した場合であっても、排ガス温度が低い(300℃以下)エンジン始動直後には触媒活性が低く、始動直後(コールドスタート時)に大量

に排出される炭化水素は浄化されずにそのまま排出されてしまうという欠点があった。この欠点を解決するため、触媒コンバータの排気上流側にコールド炭化水素を吸着するための吸着材を充填した炭化水素トラップを配置した排ガス浄化装置が提案されている(特開平2-135126号公報、特開平3-141816号公報)。

【0005】

【発明が解決しようとする課題】しかしながら、上記特開平2-135126号公報に係る排ガス浄化装置では、吸着材の下流側に触媒成分を含浸しているため、触媒が活性温度に達する前に上流側の吸着材から炭化水素が脱離してしまうと共に、ゼオライトが触媒金属溶液を含浸しているため、触媒成分の耐久性に乏しいという欠点があった。

【0006】また、特開平3-141816号公報に係る排ガス浄化装置では、吸着した炭化水素の脱離制御を温度センサ、バイパス管及び制御装置等を用いて行っているため、システムが複雑で信頼性に乏しかったり、排気レイアウト上実用的でないという欠点があった。

【0007】従って本発明の目的は、エンジン始動時に排出される高濃度の炭化水素を効率良く除去することのできる排ガス浄化用吸着触媒を提供することにある。

【0008】

【課題を解決するための手段及び作用】本発明者らは、上記課題を解決するために鋭意検討した結果、ゼオライト層上に活性セリア及び／又はアルミナを主成分とした粉末に触媒成分としてPt、Pd及びRhからなる群から選ばれた少なくとも1種を含む触媒層を有する排ガス浄化用吸着触媒を用いることにより、エンジン始動時に排出される高濃度の炭化水素を効率良く除去することのできることを見出し、本発明に到達した。

【0009】本発明の上記の目的は、触媒担体にゼオライトをコーティングした吸着触媒において、前記ゼオライト層上に活性セリア及び／又はアルミナを主成分とした粉末に触媒成分としてPt、Pd及びRhからなる群から選ばれた少なくとも1種を含む触媒層を有すること特徴とする排ガス浄化用吸着触媒により達成された。以下、本発明について更に詳細に説明する。

【0010】本発明は、上述したように触媒担体上に炭化水素を吸着するのに有効なゼオライトからなる第1層を設け、更にこの第1層上に活性セリア及び／又はアルミナを主成分とした粉末に触媒成分としてPt、Pd及びRhからなる群から選ばれた少なくとも1種を含む触媒層を設けた自己浄化型吸着触媒Aを排気流入側に、炭化水素、一酸化炭素及び窒素酸化物を浄化する三元触媒をコーティングした触媒Bを排気流出側に、それぞれ配置したことを特徴とする排ガス浄化用吸着触媒である。

【0011】流入側の吸着触媒Aは、ゼオライト層上に担持された触媒層がゼオライト層よりも早く加熱される

ため、ゼオライト層から炭化水素が脱離する段階において触媒層が活性化されており、炭化水素を良好に浄化する。また、流出側に触媒Bを配置することにより、流入側の触媒層で浄化しきれなかった炭化水素、一酸化炭素及び窒素酸化物の浄化を向上することができる。これによって排ガス中、特にエンジン始動時に排出される炭化水素を効率良く除去することができる。

【0012】本発明において使用するゼオライトとしては、公知のゼオライトの中から適宜選択して使用することができるが、特に常温から比較的高い温度で、しかも水存在雰囲気下であっても十分な炭化水素吸着能を有し、且つ高い耐久性を有するものを選択することが好ましい。このようなゼオライトとしては、例えばモルデナイト、USY、 β -ゼオライト及びZSM-5からなる群から選ばれた少なくとも1種を用いることが好ましい。特にモルデナイト、 β -ゼオライト及びZSM-5がSiO₂/Al₂O₃モル比で50~2000の範囲、USYがSiO₂/Al₂O₃モル比で50~300の範囲であることが好ましい。モルデナイト、 β -ゼオライト、ZSM-5及びUSYがSiO₂/Al₂O₃モル比で50未満になると、排ガス中に共存する水分子の吸着阻害が大きく、有効に炭化水素を吸着することができない。逆にモルデナイト、 β -ゼオライト及びZSM-5がモル比で2000を、USYがモル比で300を、それぞれ超えると、炭化水素の吸着量が減少する。細孔径や細孔構造の異なるゼオライトを2種以上混合することにより、排ガス中の多種類の炭化水素を効率良く吸収することができる。

【0013】こうして得られる吸着触媒のみでも炭化水素を十分に吸着することができるが、排気系に装着して実用化するためには温度の上昇と共に脱離する炭化水素を浄化する性能を追加した、吸着層（ゼオライト）上に三元触媒層をコーティングした自己浄化タイプとすることが好ましい。即ち、本発明においては、ゼオライト層上に活性セリア及び／又はアルミナを主成分とした粉末を塗布し、更にその粉末上に触媒成分としてPt、Pd及びRhからなる群から選ばれた少なくとも1種を含む触媒層を備えることができる。

【0014】各種ゼオライトは、H型でも十分な吸着能力を有するが、Pd、Ag、Cu、Cr、Co、Nd等をイオン交換法、含浸法、浸漬法等の通常の方法を用いて担持することにより、吸着特性や脱離抑制能をさらに向上させることができる。各貴金属の担持量は特に制限されることはないが、0.1~15重量%の範囲であることが好ましい。担持量が0.1重量%未満になると、吸着特性や脱離抑制能が低下し、逆に15重量%を超えてもそれ以上の効果は得られない。

【0015】流入側の吸着触媒Aと流出側の触媒Bとの距離は、特に制限されないが、近すぎると背圧上昇によるエンジン性能の低下を引き起こす可能性があり、逆に

離れすぎていると触媒Bの温度が上がらず脱離した炭化水素、一酸化炭素及び窒素酸化物の浄化率が低下する可能性がある。従って触媒Aと吸着触媒Bの距離は10~50mmの範囲とすることが好ましい。

【0016】本発明において触媒担体としては、公知の触媒担体の中から適宜選択して使用することができ、例えばモノリス担体やメタル担体などが挙げられる。この触媒担体の形状は、特に制限されないが、通常はハニカム形状で使用することが好ましく、ハニカム状の各種基材に触媒粉末を塗布して用いられる。このハニカム材料としては、一般にコージエライト質のものが多く用いられるが、金属材料からなるハニカムを用いることも可能であり、更には触媒粉末そのものをハニカム形状に成形しても良い。触媒の形状をハニカム状とすることにより、触媒と排気ガスの接触面積が大きくなり、圧力損失も抑えられるため自動車用として用いる場合に極めて有利である。

【0017】

【実施例】以下、本発明を実施例によって更に詳述する。実施例において特に断らない限り、部は重量部を示す。

【0018】実施例1

Ptを担持した活性セリア粉末（以下、Pt/CeO₂という）100部、アルミナ50部及び2%硝酸150部を磁性ポットに投入し、振動ミル装置で40分間、又はユニバーサルボールミル装置で6.5時間混合粉碎して、ウォッシュコートスラリーを製造した。コーディエライト製モノリス担体を吸引コート法で吸水処理した後、前記製造したスラリーを担体断面全体に均一になるように投入し、吸引コート法で余分なスラリーを除去した。次いで、乾燥を行った後、400℃で1時間仮焼成した。これによりPt/CeO₂層が100g/Lコート量で担体にコートされた。上記ウォッシュコート、乾燥、焼成をさらに繰り返して合計200g/LのPt/CeO₂層をコートした。次に、Rhを担持したアルミナ粉末（以下、Rh/Al₂O₃という）100部、アルミナ50部及び2%硝酸150部を磁性ポットに投入し、前記と同様にしてウォッシュコートスラリーを製造し、同様な方法でPt/CeO₂層上に50g/LのRh/Al₂O₃触媒層をコートし、乾燥した後、空気雰囲気下で650℃にて3時間焼成を行い、排気流出側の触媒1を得た。また、H型ZSN-5（SiO₂/Al₂O₃=700）100部、シリカゾル（固形分20%）215部、10%硝酸100部及び水15部を磁性ポットに投入し、前記と同様にしてZSM-5スラリーを製造し、同方法でモノリス担体上に150g/Lをコートし、乾燥した後、400℃にて1時間焼成を行った。前記と同様にしてZSM-5層上に100g/LのPt/CeO₂触媒層をコートし、乾燥した後、400℃にて1時間焼成を行った。更に、Pt/CeO₂層上

にRh/Al₂O₃触媒層を50g/Lコートし、乾燥した後、空気雰囲気下で650℃にて3時間の焼成を行い、排気流入側の吸着触媒1を得た。排気流入側に吸着触媒1を、排気流出側に触媒1を、それぞれ組合せてタンデム型吸着触媒1を得た。

【0019】実施例2

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例1と全く同様な方法で吸着触媒2を得、排気流入側にこの吸着触媒2を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒2を得た。

【0020】実施例3

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型ZSM-5(SiO₂/Al₂O₃=700)50部及びH型USY(SiO₂/Al₂O₃=50)50部を用いた他は、実施例1と全く同様な方法で吸着触媒3を得、排気流入側にこの吸着触媒3を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒3を得た。

【0021】実施例4

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例3と全く同様な方法で吸着触媒4を得、排気流入側にこの吸着触媒4を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒4を得た。

【0022】実施例5

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型ZSM-5(SiO₂/Al₂O₃=700)67部及びH型USY(SiO₂/Al₂O₃=50)33部を用いた他は、実施例1と全く同様な方法で吸着触媒5を得、排気流入側にこの吸着触媒5を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒5を得た。

【0023】実施例6

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例5と全く同様な方法で吸着触媒6を得、排気流入側にこの吸着触媒6を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒6を得た。

【0024】実施例7

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型ZSM-5(SiO₂/Al₂O₃=700)50部及びH型モルデナイト(SiO₂/Al₂O₃=200)50部を用いた他は、実施例1と全く同様な方法で吸着触媒7を得、排気流入側にこの吸着触媒7を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒7を得た。

【0025】実施例8

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃

を用いた他は、実施例7と全く同様な方法で吸着触媒8を得、排気流入側にこの吸着触媒8を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒8を得た。

【0026】実施例9

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型ZSM-5(SiO₂/Al₂O₃=700)50部及びH型βゼオライト(SiO₂/Al₂O₃=100)50部を用いた他は、実施例1と全く同様な方法で吸着触媒9を得、排気流入側にこの吸着触媒9を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒9を得た。

【0027】実施例10

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例9と全く同様な方法で吸着触媒10を得、排気流入側にこの吸着触媒10を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒10を得た。

【0028】実施例11

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型ZSM-5(SiO₂/Al₂O₃=700)67部及びH型βゼオライト(SiO₂/Al₂O₃=100)33部を用いた他は、実施例1と全く同様な方法で吸着触媒11を得、排気流入側にこの吸着触媒11を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒11を得た。

【0029】実施例12

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例12と全く同様な方法で吸着触媒12を得、排気流入側にこの吸着触媒12を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒12を得た。

【0030】実施例13

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型USY(SiO₂/Al₂O₃=50)100部を用いた他は、実施例1と全く同様な方法で吸着触媒13を得、排気流入側にこの吸着触媒13を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒13を得た。

【0031】実施例14

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例13と全く同様な方法で吸着触媒14を得、排気流入側にこの吸着触媒14を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒14を得た。

【0032】実施例15

ゼオライトとしてH型ZSM-5(SiO₂/Al₂O₃=700)100部に代えてH型βゼオライト(Si

7
 $O_2 / Al_2 O_3 = 100$) 100部を用いた他は、実施例1と全く同様な方法で吸着触媒15を得、排気流入側にこの吸着触媒15を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒15を得た。

【0033】実施例16

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例15と全く同様な方法で吸着触媒16を得、排気流入側にこの吸着触媒16を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒16を得た。

【0034】実施例17

ゼオライトとしてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 100部に代えてH型モルデナイト (SiO₂ / Al₂O₃ = 200) 100部を用いた他は、実施例1と全く同様な方法で吸着触媒17を得、排気流入側にこの吸着触媒17を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒17を得た。

【0035】実施例18

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例17と全く同様な方法で吸着触媒18を得、排気流入側にこの吸着触媒18を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒18を得た。

【0036】実施例19

ゼオライトとしてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 34部、H型USY (SiO₂ / Al₂O₃ = 50) 33部及びH型モルデナイト (SiO₂ / Al₂O₃ = 200) 33部を用いた他は、実施例1と全く同様な方法で吸着触媒19を得、排気流入側にこの吸着触媒19を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒19を得た。

【0037】実施例20

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例19と全く同様な方法で吸着触媒20を得、排気流入側にこの吸着触媒20を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒20を得た。

【0038】実施例21

ゼオライトとしてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 34部、H型USY (SiO₂ / Al₂O₃ = 50) 33部及びH型βゼオライトを用いた他は、実施例1と全く同様な方法で吸着触媒21を得、排気流入側にこの吸着触媒21を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒21を得た。

【0039】実施例22

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例21と全く同様な方法で吸着触媒22を得、排気流入側にこの吸着触媒22を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒22を得た。

【0040】実施例23

ゼオライトとしてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 34部、Agをイオン交換したZSM-5 (以下、Ag担持ZSM-5という。Ag担持量5重量%、SiO₂ / Al₂O₃ = 30) 33部及びH型USY (SiO₂ / Al₂O₃ = 50) 33部を用いた他は、実施例1と全く同様な方法で吸着触媒23を得、排気流入側にこの吸着触媒23を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒23を得た。

【0041】実施例24

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例23と全く同様な方法で吸着触媒24を得、排気流入側にこの吸着触媒24を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒24を得た。

【0042】実施例25

ゼオライトとしてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 34部、Pdをイオン交換したZSM-5 (以下、Pd担持ZSM-5という。Pd担持量2重量%、SiO₂ / Al₂O₃ = 30) 33部及びH型USY (SiO₂ / Al₂O₃ = 50) 33部を用いた他は、実施例1と全く同様な方法で吸着触媒23を得、排気流入側にこの吸着触媒23を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒23を得た。

【0043】実施例26

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例25と全く同様な方法で吸着触媒26を得、排気流入側にこの吸着触媒26を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒26を得た。

【0044】実施例27

ゼオライトとしてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂ / Al₂O₃ = 700) 34部、Ag担持ZSM-5 (Ag担持量5重量%、SiO₂ / Al₂O₃ = 30) 33部、H型βゼオライト (SiO₂ / Al₂O₃ = 100) 33部を用いた他は、実施例1と全く同様な方法で吸着触媒27を得、排気流入側にこの吸着触媒27を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒27を得た。

【0045】実施例28

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例27と全く同様な方法で吸着触媒28を得、排気流入側にこの吸着触媒28を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒28を得た。

【0046】実施例29

ゼオライトとしてH型ZSM-5 (SiO₂/Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂/Al₂O₃ = 700) 34部、Pd担持ZSM-5 (Pd担持量2重量%、SiO₂/Al₂O₃ = 30) 33部、H型βゼオライト (SiO₂/Al₂O₃ = 100) 33部を用いた他は、実施例1と全く同様な方法で吸着触媒29を得、排気流入側にこの吸着触媒29を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒29を得た。

【0047】実施例30

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例29と全く同様な方法で吸着触媒30を得、排気流入側にこの吸着触媒30を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒30を得た。

【0048】実施例31

ゼオライトとしてH型ZSM-5 (SiO₂/Al₂O₃ = 700) 100部に代えてH型ZSM-5 (SiO₂/Al₂O₃ = 700) 50部及びAgをイオン交換したUSY (以下、Ag担持USYという。Ag担持量5重量%、SiO₂/Al₂O₃ = 12) 50部を用いた他は、実施例1と全く同様な方法で吸着触媒31を得、排気流入側にこの吸着触媒31を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒31を得た。

【0049】実施例32

触媒成分としてPt/CeO₂に代えてPd/Al₂O₃を用いた他は、実施例31と全く同様な方法で吸着触媒32を得、排気流入側にこの吸着触媒32を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒32を得た。

【0050】実施例33

実施例1と同様な方法でPd/CeO₂層を200g/Lコートし、乾燥した後、焼成を行った。更に、同様な方法でPd/CeO₂層上にRh/Al₂O₃層を50g/Lコートし、乾燥した後、空気雰囲気下で650℃にて3時間焼成を行い、触媒2を得た。排気流入側に吸

着触媒5を、排気流出側に触媒2を、それぞれ組み合わせてタンデム型吸着触媒33を得た。

【0051】実施例34

排気流入側に吸着触媒9を、排気流出側に触媒2を、それぞれ組み合わせてタンデム型吸着触媒34を得た。

【0052】実施例35

触媒成分としてPt/CeO₂に代えてPt/CeO₂及びPd/Al₂O₃を用いた他は、実施例3と全く同様な方法で吸着触媒35を得、排気流入側にこの吸着触媒35を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒35を得た。

【0053】実施例36

ゼオライトとしてH型ZSM-5 (SiO₂/Al₂O₃ = 700) 50部及びH型USY (SiO₂/Al₂O₃ = 50) 50部に代えてH型ZSM-5 (SiO₂/Al₂O₃ = 700) 67部及びH型USY (SiO₂/Al₂O₃ = 50) 37部を用いた他は、実施例35と全く同様な方法で吸着触媒36を得、排気流入側にこの吸着触媒36を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒36を得た。

【0054】比較例1

H型USY (SiO₂/Al₂O₃ = 50) 100部、シリカゾル (固形分20%) 215部、10%硝酸100部及び水15部を磁性ボットに投入し、実施例1と全く同様な方法でウォッシュコートスラリーを製造し、同コート方法でモノリス担体に150g/Lコート、乾燥、焼成を行い、吸着触媒37を得た。排気流入側に吸着触媒37を、排気流出側に触媒1を、それぞれ組み合わせてタンデム型吸着触媒37を得た。

【0055】比較例2

H型USY (SiO₂/Al₂O₃ = 50) に代えてH型USY (SiO₂/Al₂O₃ = 7) を用いた他は、比較例1と全く同様な方法により、吸着触媒38を得、排気流入側にこの吸着触媒38を、排気流出側に実施例1で得た触媒1を、それぞれ組合せてタンデム型吸着触媒38を得た。

【0056】試験例

実施例1～34及び比較例1～2で得られたタンデム型吸着触媒を用いて下記評価条件でHC吸着・洗浄特性の評価を行った。その結果を表1、2及び3に示す。

【0057】

【表1】

	触媒番号	H C低減率 Abag 0~125 秒	H C低減率 Abag 0~505 秒
実施例 1	吸着触媒 1	38.8%	6.1%
実施例 2	同 2	38.8%	6.4%
実施例 3	同 3	51.3%	15.2%
実施例 4	同 4	51.3%	17.6%
実施例 5	同 5	51.8%	15.5%
実施例 6	同 6	51.8%	17.7%
実施例 7	同 7	41.7%	13.0%
実施例 8	同 8	41.7%	13.3%
実施例 9	同 9	51.9%	17.7%
実施例 10	同 10	51.9%	17.8%
実施例 11	同 11	52.3%	17.9%
実施例 12	同 12	52.3%	18.1%
実施例 13	同 13	39.4%	12.9%
実施例 14	同 14	39.4%	13.1%
実施例 15	同 15	45.0%	15.1%
実施例 16	同 16	45.0%	15.3%
実施例 17	同 17	39.0%	9.0%

【0058】

【表2】

	触媒番号	H C低減率	H C低減率
実施例 18	吸着触媒 18	39.0%	9.1%
実施例 19	同 19	52.0%	15.1%
実施例 20	同 20	52.0%	15.2%
実施例 21	同 21	52.5%	18.1%
実施例 22	同 22	52.5%	18.2%
実施例 23	同 23	52.9%	18.5%
実施例 24	同 24	52.9%	18.6%
実施例 25	同 25	51.4%	15.3%
実施例 26	同 26	51.4%	17.7%
実施例 27	同 27	53.1%	18.9%

【0059】

【表3】

	触媒番号	H C低減率	H C低減率
実施例 28	吸着触媒 28	53.1%	18.9%
実施例 29	同 29	51.5%	15.3%
実施例 30	同 30	51.4%	15.3%
実施例 31	同 31	52.0%	15.4%
実施例 32	同 32	52.0%	15.6%
実施例 33	同 33	51.8%	16.8%
実施例 34	同 34	51.9%	17.9%
実施例 35	同 35	51.3%	16.5%
実施例 36	同 36	51.3%	14.8%
比較例 1	同 37	39.4%	0%
比較例 2	同 38	2.0%	0%

30

40 【0060】尚、評価に当たっては図1に示すようにエンジン1のエキゾーストマニホールド2にブリ三元触媒3(0.5L)としてPt-Pb系触媒を配置し、床下触媒5(1.3L)のPt-Rh系触媒の前に吸着触媒4(1.3L)を装着した排ガス浄化装置を用い、吸着触媒未装着の場合と性能比較を行った。評価に当たっては、

(1) エンジン始動時に排出される炭化水素の吸着能を評価するためAbag0~125秒間のエミッション低減率を測定した。

50 (2) 一時的に吸着した炭化水素も吸着触媒下流の三元

触媒が活性化する前に脱離して エミッション低減効果がない。そこで吸着触媒による脱離抑制能及び自己浄化能を評価するためAbaq0～505秒間のエミッション低減率を測定した。

【0061】評価条件

触媒容量 1.3L

評価車両 日産自動車株式会社製、V型6気筒3000ccエンジン

評価モード LA4-CH(Abag)

エンジン始動時に排出される(触媒入口のガス中の)炭化水素

炭素数 $C_1 \sim C_3$ 21.2% (C_1 成分除く)

$C_4 \sim C_6$ 33.0%

$C_7 \sim C_9$ 45.8%

【0062】

*【発明の効果】本発明の排ガス浄化用吸着触媒は、触媒担体上に炭化水素吸着に有効な吸着層上に触媒層がコートされた吸着触媒を排気流入側に配置し、触媒担体上に触媒活性成分を含む無機物をコートした触媒を排気流出側に配置することにより、エンジン始動時に排出される高濃度の炭化水素を効率良く除去することのできる。

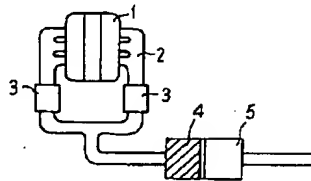
【図面の簡単な説明】

【図1】試験例に用いた排ガス浄化装置の系統図である。

【符号の説明】

- 1 エンジン
- 2 エキゾーストマニホールド
- 3 プリ三元触媒
- 4 吸着触媒
- * 5 床下三元触媒

【図1】



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